



# Pyrolysis of black liquor for phenols and impact of its inherent alkali



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## ABSTRACT

This study is devoted to investigating the potential of producing phenols via pyrolysis of lignin in black liquor (BL) by a fixed bed reactor at 350–550 °C. The chemicals in the pyrolysis liquid of both black liquor solid (BLS) and purified lignin (PL) from BL are mainly phenols including 4-methoxyphenol, 3,4-dimethoxyphenol, 2-methoxy-4-alkylphenols and alkylphenols. For pyrolysis of BLS, high temperature facilitated the breakage of methoxyl group(s). The highest liquid yield was 27 wt.% at 450 °C, and the content of phenols free of -OCH<sub>3</sub> reached 55 wt.% in addition to a small amount of other phenols. The pyrolysis of PL with and without addition of alkali additives of NaOH and Na<sub>2</sub>CO<sub>3</sub> at 450 °C verified that the alkali could promote the formation of phenols. The strong alkali of NaOH greatly promoted the production of phenols free of -OCH<sub>3</sub>, whereas the effect of Na<sub>2</sub>CO<sub>3</sub> in this aspect was much less. Catalyzed by its self-contained alkalis, the pyrolysis of BLS had high contents of alkylphenols and phenol in the tar (organics). This shows the prospective for production of phenols from pyrolyzing black liquor, while the heating value of the pyrolysis residue was above 6300 kJ/kg to further support the cascade utilization of BLS.

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## 1. Introduction

Nowadays more biomass wastes including agricultural and industrial sources are becoming the effective supplement of energy and chemical materials. Black liquor (BL) comes out as a by-product from commercial pulping processes of papermaking industry, and it is the spent solution from cooking wood chips in the aqueous solution of sodium hydroxide and sulfide [1,2]. Annually about 240 million tons of black liquor is produced worldwide and is being considered as an important and concentrated biomass resource [1]. The major organic matters in BL are lignin (usually alkali lignin in China because of the wide use of alkali such as soda in pulping processes), hemicellulose, a small amount of cellulose and some other extractives. Its inorganic compounds are mainly the recyclable pulping alkali and salts [3,4]. Drying or dewatering can make the solid content of the condensed BL to be 15 wt.% to 60 wt.%, sometimes even to 80 wt.% in a multi-stage evaporation or assisted with micro wave evaporation [5–7]. The high organic as well as alkaline content, BL is actually the most serious industrial water pollution [1,8]. Being a by-product, so far BL is only occasionally treated to produce some low-value products such as dispersants or binding agents [9–11]. In most cases BL is simply burned to recover energy and alkali in, for example, the so-called Tomlinson recovery boilers [7,12,13]. Although the way of alkali recovery via combustion is widely adopted in industry, its realized utilization value is low, while its involved boilers are also facing serious deposition

problems of inorganic alkali and salts on the surfaces of furnace and heat-exchanger to cause serious corrosion, quick drop in heat transfer efficiency and equipment reliability [14,15].

BL gasification (BLG) has been suggested to be a more value-added way for utilizing BL. Reports are available for gasification of BL by steam gasification [7,16], supercritical water gasification [6,17] and pyrolysis gasification [5,18]. The BLG can support the combined cycle of electricity generation to realize high efficiency [19]. In gasification, the organic matters in BL are converted into a clean gas fuel suitable for gas turbine [20]. The BLG can also be applied to productions of hydrogen, methanol, DME, FT diesel, substitute nature gas (SNG) and so on [7,21–23]. These biobase fuels are potential to decrease our heavy dependence on fossil fuels and to reduce the environment impacts including the emission of CO<sub>2</sub>. Consonni et al. [13] have integrated pulpmill biorefineries based on gasification of black liquor and wood residue and deeply analyzed the possible production of biofuels including mixed-alcohols, dimethyl ether and FT liquid.

Nonetheless, via BLG it cannot use the value of the aromatic structure present in the lignin of BL. Lignin, as the most abundant natural aromatic polymer, has highly branched three-dimensional phenolic structure consisting of three main phenylpropane units including p-coumaril, coniferyl and sinapyl. Thus, the lignin in BL is highly suitable for production of value-added aromatic chemicals such as phenols required by many chemical processes like synthesis of phenol formaldehyde resin and plastics [24–27]. This is significant especially considering the natural abundance of BL lignin. Pyrolysis provides the best way to extract the high-value aromatic structure from BL through its degrading the lignin into oligomers, even monomers but remaining

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its inherent aromatic structure. Via pyrolysis, it allows the implementation of cascade utilization of alkaline BL. It implements actually the cascade utilization of alkaline BL because the residue of pyrolysis can be combusted or gasified like the original BL.

By far, only limited studies have been conducted for phenols by pyrolysis of BL, but most studies are about kinetics [3,22] and char characteristics [8,12,18,28], while tremendous literature studies on lignin pyrolysis are mainly for lignin from other natural biomass or for other extracted lignin [25,29–33]. Considering the alkali-containing nature of BL, this study intends to investigate the effect of self-containing alkalis (usually NaOH and  $\text{Na}_2\text{CO}_3$ ) on the pyrolysis of alkaline BL and to clarify what and how many chemicals can be potentially produced via pyrolysis of BL. For this, pyrolysis tests will be carried out for solid from dried alkaline BL in a fixed bed reactor at different temperatures. The results will be further compared with those from pyrolyzing the purified lignin of BL (alkali removed) with and without addition of NaOH and  $\text{Na}_2\text{CO}_3$  to clarify the effects of the alkali containing in BL. The heating value of the solid residue or char from pyrolyzing BLS (black liquor solid) is also analyzed to show the feasibility of its combustion and gasification that is basic for the pyrolysis-leading cascade utilization of BLS.

## 2. Experimental

### 2.1. Apparatus and methods

As Fig. 1 shows, the pyrolysis experiments were all performed in a quartz fixed bed reactor in nitrogen atmosphere as previous work [34]. The reactor had an internal diameter of 30 mm and a length of 400 mm. A sintered quartz plate at 200 mm above the reactor lower end supported the tested materials. The reactor was externally heated using an electric furnace, and the reaction temperature was controlled via a PID controller. Nitrogen was used as the carrier gas, and its flow was monitored using a mass flow controller. The  $\text{N}_2$  flow was preheated in a gas preheater. The produced pyrolysis gas first passed through two coil condensers immersed in an ice-water bath to obtain the liquid product. The uncondensed gas was further cleaned, in succession, with acetone adsorption also in an ice-water bath, a filter and a silica gel column to get the final gas, which was ultimately collected in gas bags for analysis.

The pyrolysis test was conducted in a similar procedure as presented in reference [34]. It was started by placing a certain amount (5 g) of

tested sample into the feed hopper. Heating the reactor and setting the  $\text{N}_2$  flow rate to 20 mL/min were in turn performed. When the desired temperatures of the reactor were reached, the BLS was fed into the bed to initiate the pyrolysis through instantaneously opening the valve of the overhead fuel hopper. The produced pyrolysis gas was treated through the condensation and cleaning steps mentioned above to get the pyrolysis liquid and clean gas for analyses. The produced pyrolysis liquid amount was determined by the mass difference of the coil condensers before and after a pyrolysis test. The collected liquid was well layered, and the water-soluble fraction was acquired by decantation, while the water-insoluble oil was recovered through washing the reactor and condenser using acetone followed with dehydration by  $\text{MgSO}_4$  and rotating evaporation of the solvent under a reduced pressure. The yield of organics was the difference between the liquid and water. It was found that the total mass balance was in the range of 90–95 wt.%, and the results presented herein in this article were all normalized to 100%.

### 2.2. Analysis approach and material

The pyrolysis gas was analyzed in a micro GC (Agilent 3000A) for its molar composition, and its volume was determined by taking the well-metered nitrogen flow as the tracer gas (its fraction in the gas product was given by GC). The composition of the pyrolysis liquid was measured using a GC-MS (VARIAN) that adopted a high-purity helium stream as the carrier gas. The reported content of each component in the pyrolysis liquid was calculated as the relative peak area ratio against the total peak area (excluding that of solvent) of a total ion chromatogram (TIC) of GC-MS result. The validity of this approach has already been verified in our previous work [34].

The water content in the water-layer solution obtained from separating the liquid product into oil and water was measured using a Karl Fischer titrator (Metrohm 870 KF Titrino plus). FTIR spectra of the BLS and PL and their chars from pyrolysis were recorded on a Bruker FTIR spectrophotometer (Tensor 27) using KBr pellet containing 1 wt.% sample. The scanning wave length was in the range of  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . Heating values of BLS and char from BLS pyrolysis were analyzed using an automatic calorimeter (SCLR-5000).

All yields presented in this article refer to the mass percentages of the products to the mass of the lignin fed into the reactor in each test. For analysis of the tested material, the pyrolysis behavior was first studied in a TGA, which was first heated at  $20\text{ }^\circ\text{C/min}$  to  $120\text{ }^\circ\text{C}$  for removing moisture and then at  $10\text{ }^\circ\text{C/min}$  to  $1000\text{ }^\circ\text{C}$  for characterizing the pyrolysis. The gas atmosphere for the TGA tests was also high-purity nitrogen at a flow rate of 100 mL/min.

The tested raw materials included the BLS and purified lignin (PL) from black liquor (BL). The BLS was obtained by drying the BL from soda pulp of wheat straw at  $105\text{ }^\circ\text{C}$ . The PL was free of NaOH and  $\text{Na}_2\text{CO}_3$  as well as phenolic salts and was prepared through treating BL according to the following steps [34,35]. The BL was first precipitated by adjusting its pH value to about 2.0 using 10%  $\text{H}_2\text{SO}_4$ , and the precipitated solid was in turn centrifugally separated from acid solution. After thoroughly washing the resulting solid with distilled water, the remaining solid was dried and dissolved into 1,4-dioxane and filtered to remove inorganic impurities. It was finally reclaimed by, in succession,

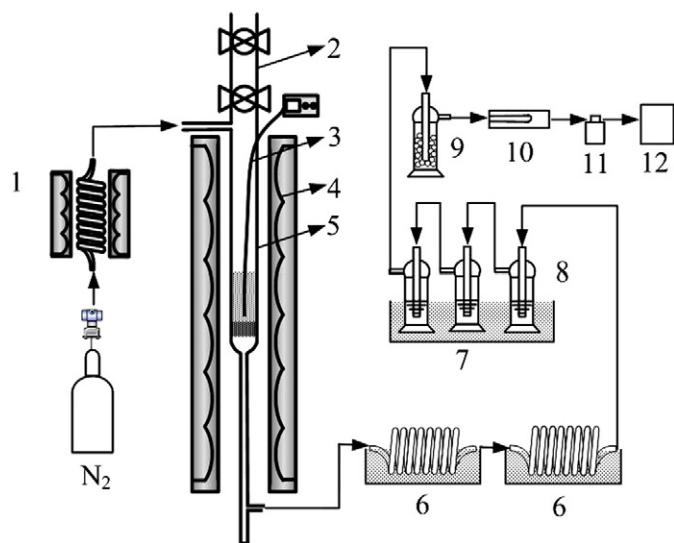


Fig. 1. A schematic diagram of the employed fixed bed pyrolysis apparatus. (1. Gas preheater, 2. Feeder, 3. Thermocouple, 4. Furnace, 5. Reaction tube, 6. Condenser, 7. Ice-water bath, 8. Acetone absorption, 9. Drier, 10. Filter, 11. Pump, 12. Gas bag.)

Table 1  
Proximate and ultimate analyses (wt.%) of the tested materials.

Lignin type	Proximate analysis				Ultimate analysis (daf)				
	$M_{ad}$	$A_d$	$V_{daf}$	$FC_{daf}$	C	H	N	S	O <sup>a</sup>
BLS	14.39	26.74	88.35	11.65	39.84	3.03	0.31	0.64	56.18
PL	6.49	0.73	65.97	34.03	59.28	5.37	0.70	1.27	33.38

daf: dry and ash-free base;  $M_{ad}$ : moisture (air dried base);  $A_d$ : ash (dry base, i.e., moisture free base);  $V_{daf}$ : volatile matter (dry and ash-free base);  $FC_{daf}$ : fixed carbon (dry and ash-free base); a by difference. The method is referring to [36].

rotary vacuum evaporation of solvent, water washing, vacuum filtration and drying at 75 °C.

As Table 1 lists, the BLS has obviously higher ash content, while the PL has the higher fixed carbon content and contains less oxygen but more carbon. These differences in fuel properties are due to not only the removal of ash from BLS in making PL but also to the fact that some oxygen-containing small-molecule compounds were removed through water washing and vacuum filtration in PL preparation. Usually, the small-molecule organic compounds contain more oxygen and less carbon.

### 3. Results and discussion

#### 3.1. FTIR and TG analysis for raw materials

As shown in Fig. 2 and Table 2, all peaks below 1000 cm<sup>-1</sup> typify the deformation vibrations of C-H bonds associates with aromatic rings, while the absorption band at the wavenumber around 3430 cm<sup>-1</sup> corresponds to the strong O-H stretching vibration, indicating the presence of phenols or alcohols or carboxyl acids in BLS and PL [37]. A more significant peak at 2930 cm<sup>-1</sup>, which represents the C-H bond stretching vibration in methyl and methylene groups, appeared stronger in PL than in BLS. This implies that both methyl and methylene groups in C<sub>3</sub> branched chains are greatly condensed in preparing PL. The stretching vibration at 1715–1705 cm<sup>-1</sup> indicating the existence of C = O in ketones, carboxylic acids or aldehydes obviously present in PL but not in BLS. For PL, the peak at 1605 cm<sup>-1</sup> is evident, revealing the aromatic skeletal vibrations plus C = O stretching vibration. All the peaks mentioned above are presented in the FTIR spectra of PL and BLS, but they are more conspicuous in PL, as a result of the component changes depicted above and the partial removal of ash from BLS during the preparation of PL [29,37–40].

The mass loss continued for both BLS and PL until the tested highest temperature of 1000 °C. As shown in Fig. 3, their ultimate residues at the similar ending temperature of 1000 °C were about 21% and 35% of their original sample masses, respectively. For PL, the most significant mass loss happened at 120–700 °C with a wide DTG peak centered at 320 °C to indicate the lignin decomposition. A small mass loss of about 7% below 120 °C should correspond to the dehydration of PL, and the invisible mass loss above 700 °C meant the reactions of coking or char condensation. In comparison, the DTG curve for BLS is obviously more complex due to its more complex composition than that of PL. Considering the pyrolysis stage of organic matters, it occurred also at 120–700 °C and the mass losses with DTG peaks at about 250, 330 and 450 °C roughly corresponded to the degradation of C<sub>3</sub> branched chains, cleavage of ether bonds between aromatic monomers and

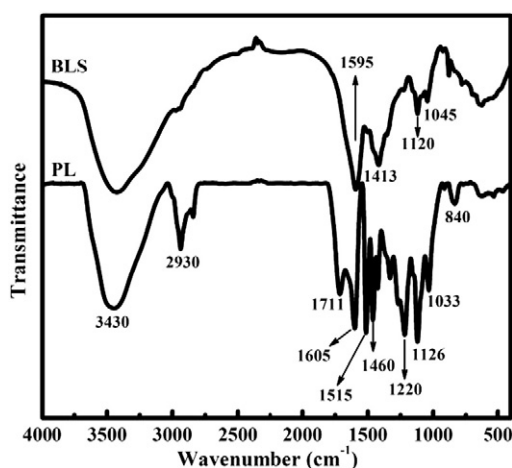


Fig. 2. FTIR spectra for the tested BLS and PL samples.

**Table 2**  
Major FTIR spectral assignment for BLS and PL.

Wavenumber (cm <sup>-1</sup> )	Assignment
834	C-H out of plane
1100–1030	C-O deformation in primary alcohols; aromatic in plane
1270–1220	C-H deformation; C = O stretch
1500–1300	C-O vibration plus C = O stretch plus C-C in guaiacyl and syringyl rings
1650–1600	C-H vibration
1715–1705	Aromatic skeletal vibration plus C = O stretch
2930	C = O stretch in carboxylic acids, ketones and aldehydes
2930	C-H stretch in methyl and methylene groups
3430	O-H stretch in phenols, alcohols and water

removal of methoxyl groups, respectively. The DTG peak at about 150 °C could be explained with the decomposition of organic impurities that are usually some small-molecular compounds such as hemicellulose. Overall, there was another big mass loss after 700 °C, which denotes the condensation of char (deep removal of H and O elements) and decomposition of inorganic salts such as sodium carbonate [1, 18,28]. Also, the carbonate in BLS may react with carbon to form volatilizing alkaline metal (such as sodium) and CO to incur certain mass loss, for instance, by  $2C + Na_2CO_3 \rightarrow 2Na + 3CO$  [41]. These caused then the two distinctive DTG peaks shown at 720 °C and 850 °C for the char condensation and salt decomposition, respectively. Because of the salt decomposition and alkaline metal vaporization, in Fig. 3 the high-ash BLS had conversely the lower residue mass of 21 wt.% in comparison with 35 wt.% for PL.

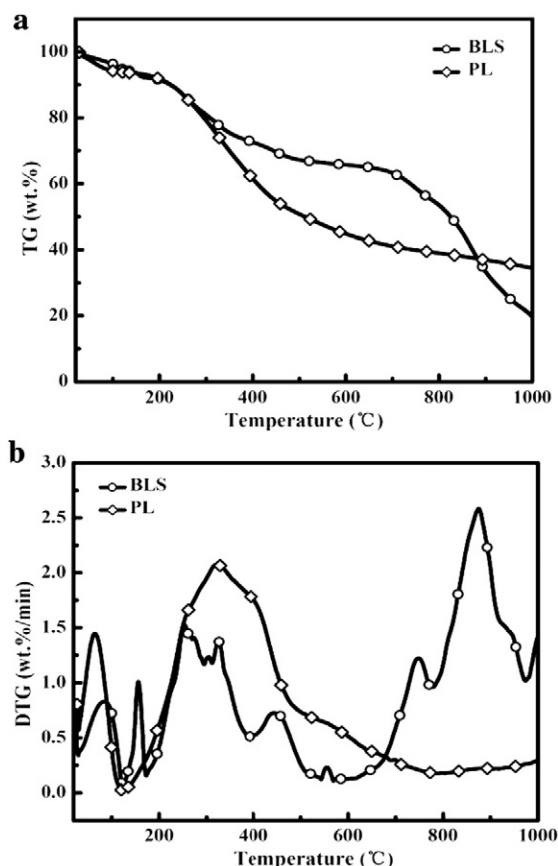


Fig. 3. TG and DTG diagrams in N<sub>2</sub> for BLS and PL.

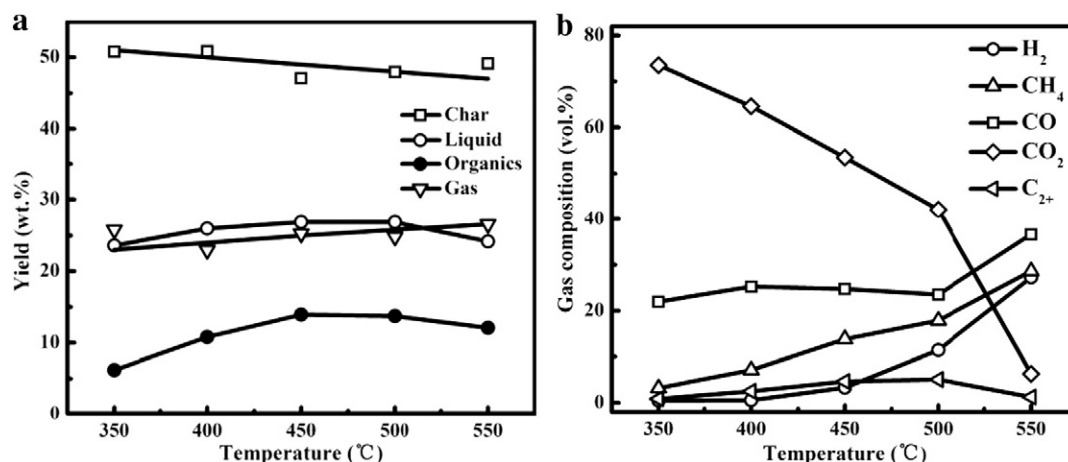


Fig. 4. Results of pyrolyzing BLS at different temperatures (a) product distribution and (b) gas composition.

### 3.2. Pyrolysis of BLS

Fig. 4 shows that the char yield of BLS pyrolysis was highest and ranged in 48–51 wt.% from 350 °C to 550 °C. The yields of liquid (including water and organics) and gas were comparative, and both varied in 24–29 wt.%. Carefully examining the variations one can find that the liquid yield slightly increased first and then decreased after 500 °C, while the gas yield was almost stable. The highest liquid yield was 27 wt.% between 450 °C and 550 °C. The yield of organic compounds or bio-oil (tar) in the liquid was calculated by subtracting water content from the liquid yield. It varied in 6–14 wt.% and reached its highest value of about 14% at 450–500 °C. As for gas compositions, increasing temperature formed more H<sub>2</sub>, CH<sub>4</sub> and CO, whereas the concentration of CO<sub>2</sub> continuously decreased and that of C<sub>2+</sub> gases first slightly increased and then decreased. The CH<sub>4</sub> formation is mostly related to methoxyl group(s) and its continuous increase with raising temperature indicates the gradually significant removal of methoxyl group(s). Hydrogen comes mainly from cracking of side-chains and

–OCH<sub>3</sub> at low temperatures or from polymerization and condensation of aromatic rings at high temperatures. The content of C<sub>2+</sub> gas started to decrease since 500 °C, implying that these gas species may crack further at high temperatures.

The major chemical species identified from the chromatogram in Fig. 5 are listed in Table 3. The major ones are 4-methoxyphenol, phenol, 3,4-dimethoxyphenol, alkylphenols, 2-methoxy-4-alkylphenol, dimethoxybenzene. Of them, the alkylphenols include further cresol, ethylphenol and xylene.

Fig. 6 compares the contents of major chemicals by the same approach of our previous work [34]. With increasing temperature from 350 °C to 550 °C, the contents of all the phenols having –OCH<sub>3</sub> attached to aromatic rings, including 4-methoxyphenol, 2-methoxy-4-alkylphenols and 3,4-dimethoxyphenol, obviously decreased, and their total content decreased from about 40% to about 3%. In comparison, the phenols free of –OCH<sub>3</sub> including phenol and alkylphenols kept their high total content at about 60%, although at 350 °C the content of alkylphenols was relatively low. At 450–550 °C, the alkylphenols showed the highest content, just corresponding to the highest organics yield. As temperature rises, the species with less –OCH<sub>3</sub> group were detected, indicating the higher extent of deoxygenation for lignin at higher temperatures.

Comparing with the FTIR spectrum of BLS in Fig. 3, the absorption peaks for the chars in Fig. 7 are much simpler than for the raw BLS, and increasing temperature makes the spectrum have weaker and fewer characteristic peaks. The absorption peak at 3430 cm<sup>–1</sup> characterizing the –OH stretching vibration significantly decreased after the pyrolysis, and above 450 °C it almost disappeared [37,42]. This indicates the removal of alcoholic groups in branched chains by pyrolysis (not phenols and carboxylic acids because they mostly exist as the form of phenolates and carboxylates in BLS). The characteristics of the peak at about 1576 cm<sup>–1</sup> indicates clearly that carbonyl and/or carboxylic groups were removed by pyrolysis and the removal was thorough at temperatures above 450 °C. This suggests that high temperature promoted decarboxylation or decarbonylation reactions, and carboxylic and carbonyl groups were broken to form gradually more CO, as is shown in Fig. 4. The peaks at 1440 cm<sup>–1</sup> and 876 cm<sup>–1</sup> are mainly characteristic absorptions due to sodium carbonate, revealing that its content increased with increasing the temperature from 350 °C to 550 °C.

In summary, for the pyrolysis of BLS in N<sub>2</sub>, the suitable temperature for producing organics or tar is 450–550 °C, and phenol and alkylphenols take up the majority (about 60%) of the tar (organics) components in addition to small amounts of 4-methoxyphenol, 2-methoxy-4-alkylphenol and 3,4-dimethoxyphenol. The highest organics or tar yield can reach about 14 wt.% of the treated lignin, while char is about 50% and gas is about 25 wt.% (the other is water). In the formed gas at 450–550 °C,

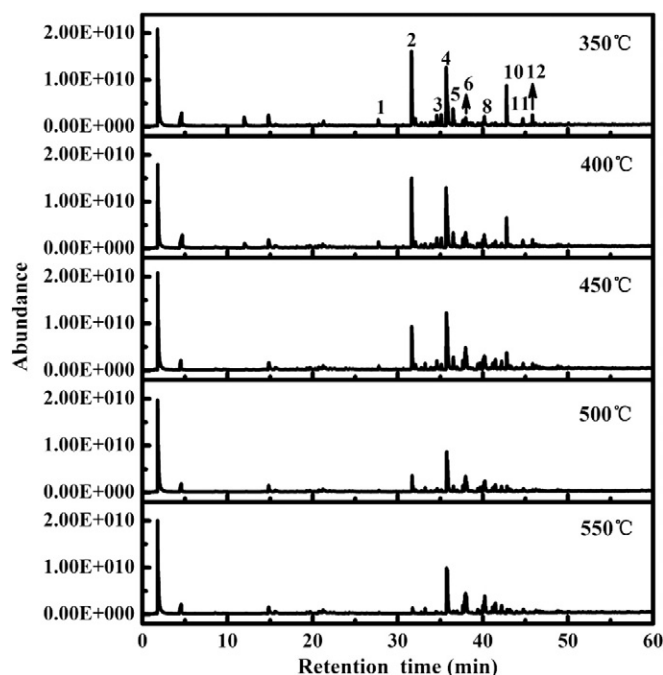
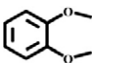

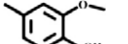
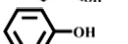
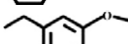

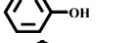
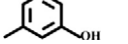
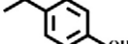
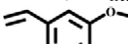
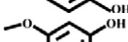
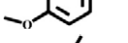
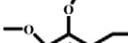

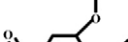
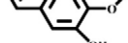
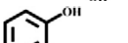


Fig. 5. Total ion chromatograms of tar (organics) from pyrolyzing BLS at different temperatures (chemicals for peaks 1 to 12 being in Table 3).



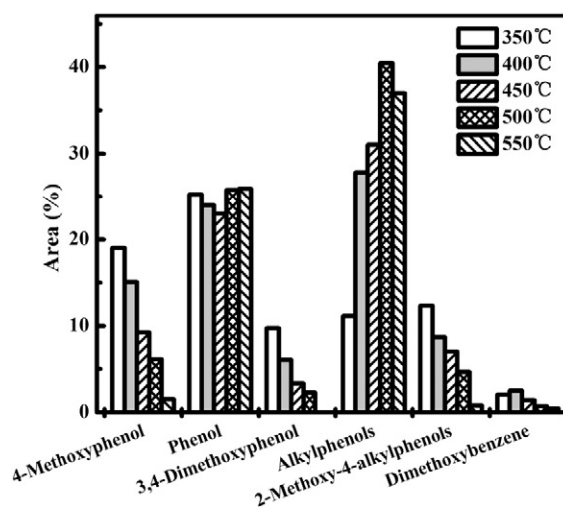
**Table 3**

Characterization of chemicals in bio-oil based on Figs. 5 and 10 for pyrolysis of BLS and PL with and without additives.

Peak no.	RT (min)	Name of compound	Structure
1	27.73	1,2-Dimethoxybenzene	
2	31.63	4-Methoxyphenol	
3	34.60	2-Methoxy-4-cresol	
4	35.70	Phenol	
5	36.52	2-Methoxy-4-ethylphenol	
6	37.99	2,3-Xylenol	
7	38.06	3-Cresol	
8	40.19	4-Ethylphenol	
9	40.89	2-Methoxy-4-vinylphenol	
10	42.79	3,4-Dimethoxyphenol	
11	44.71	(2,3-Dimethoxyphenyl)methanol	
12	45.84	3-Hydroxy-4,5-dimethoxybenzaldehyde	
13	47.75	3-Methoxy-1,2-benzenediol	
14	49.47	6-Hydroxy-4-methoxy-2,3-xylenaldehyde	
15	50.71	1-(4-Hydroxy-3-methoxyphenyl)ethanone	
16	51.62	1,4-Benzenediol	
17	57.59	1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone	

CO<sub>2</sub> takes about 50 vol.%, CO about 25 vol.% and CH<sub>4</sub> 15–20 vol.%, while H<sub>2</sub> and C<sub>2+</sub> species have low contents. At these temperatures the salts from BL are stable and remain in the char.

As Fig. 8 demonstrates, the BLS had an HHV of about 9700 kJ/kg, and it can be fuels for gasification, combustion and many others [13,23]. The heating value of the char was lower than the BLS, and it decreased with increasing the pyrolysis temperature but was above 6300 kJ/kg. Consequently, the char can be well combusted to recover energy and alkalis containing in BL, showing the technical feasibility for the proposed cascade utilization of BLS by pyrolysis first to produce value-added



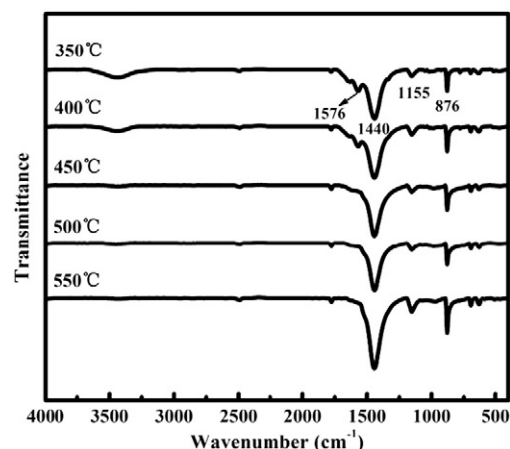
**Fig. 6.** Content comparison for major chemicals in tar (organics) from pyrolysis of BLS at different temperatures (based on Fig. 5).

chemicals as well as gas and in turn combustion of the char to recover energy and alkalis.

### 3.3. Pyrolysis of PL

In order to understand the effects of the self-containing alkalis on the pyrolysis of BLS, pyrolysis of PL was performed in the same facility for both cases with and without alkaline additives. The additive was physically mixed into PL. According to the preceding results, the reaction temperature was set at 450 °C for having the higher tar (organics) yield. Comparing to BLS pyrolysis, the pyrolysis of pure PL without additive in Fig. 9 led to the higher yields of liquid, organics (i.e., bio-oil or tar) and char but the lower gas yield. The condensed phenolates and carboxylates by reacting with sodium salts in PL are possibly easy to transform into phenols and carboxylic acids which are easier to volatilize into chemicals and gas. On the other hand, the catalytic effect of ash and alkalis present in BLS would facilitate the formation of pyrolysis gas, especially considering that the alkalis are more dispersed than the alkali physically mixed into PL (see comparison herein).

The chromatogram in Fig. 10 shows clearly that the formed chemicals are obviously more complicated for PL pyrolysis than for the pyrolysis of BLS. While all chemicals corresponding to the peaks 1 to 17 can be identified for the tar (organics) of PL pyrolysis, only part of such chemicals were found in the chromatogram of BLS pyrolysis. Fig. 11 shows that in the tar (organics) of PL pyrolysis



**Fig. 7.** FT-IR spectra of the chars from BLS pyrolysis at different temperatures.

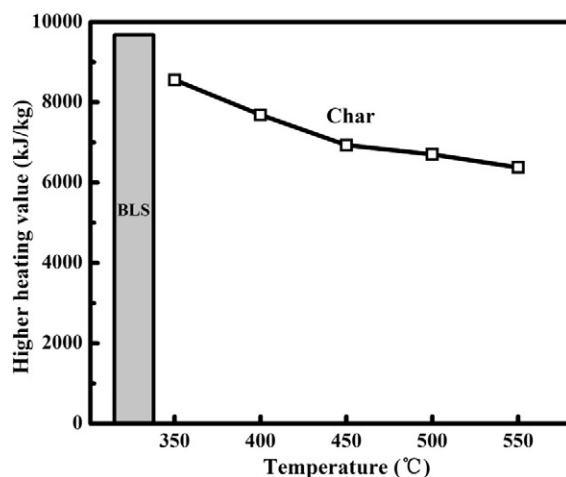


Fig. 8. HHV of BLS and char from BLS pyrolysis at different temperatures.

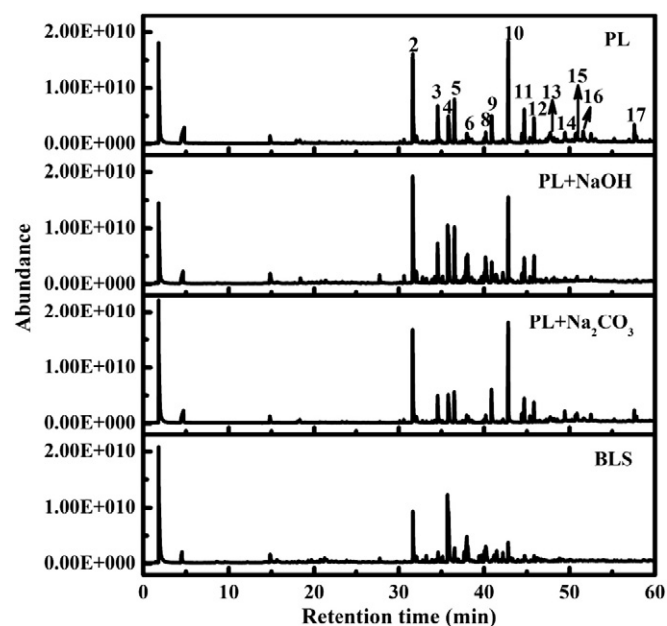


Fig. 10. Total ion chromatograms of tar (organics) from pyrolyzing BLS and PL with and without an additive at 450 °C (chemicals for peaks 1 to 17 are in Table 3).

there were more phenols containing methoxyl group(s) including 4-methoxyphenol, 3,4-dimethoxyphenol and 2-methoxy-4-alkylphenols but fewer alkylphenols and phenol free of methoxyl group(s) in comparison with that of BLS pyrolysis. For BLS pyrolysis, the dominant chemicals were phenol (23%) and alkylphenols (31%), whereas for the pyrolysis of PL without any additive, the contents of 4-methoxyphenol, 3, 4-dimethoxyphenol and 2-methoxy-4-alkylphenols were all about 15%. Presumably, the self-containing alkalis as well as ash in BLS promoted the cracking of tar (organics) species and

the break of methoxyl groups in the generated tar (organics). For both PL and BLS, the major pyrolysis gas species were  $\text{CH}_4$  (~20 vol.%),  $\text{CO}$  (~20 vol.%) and  $\text{CO}_2$  (~50 vol.%), while the PL pyrolysis had relatively higher  $\text{CH}_4$  content and lower  $\text{CO}$  and  $\text{CO}_2$  contents in its pyrolysis gas.

Pyrolysis of PL with an additive of NaOH or  $\text{Na}_2\text{CO}_3$  was conducted to reveal the effect of alkaline additive on the formed products. Since BLS had some ash, the mixed alkaline additive for PL was 20 wt.% of the PL. The results are compared in Figs. 9 to 12. Comparing with pyrolysis of PL alone, the use of additive little varied the yield of liquid (with water) but decreased the organics (bio-oil or tar) yield. There was an obviously lower gas yield with NaOH additive, while the use of  $\text{Na}_2\text{CO}_3$  slightly increased the gas yield. Nonetheless, the gas yield in all cases related to PL was obviously lower than that of BLS pyrolysis. This means that the alkaline ash in BLS greatly impacted the pyrolysis to result in more gas. Furthermore, Fig. 9 reveals that adding NaOH and  $\text{Na}_2\text{CO}_3$  respectively increased and decreased the char yield, but the yield was still higher than that of BLS pyrolysis. Considering the

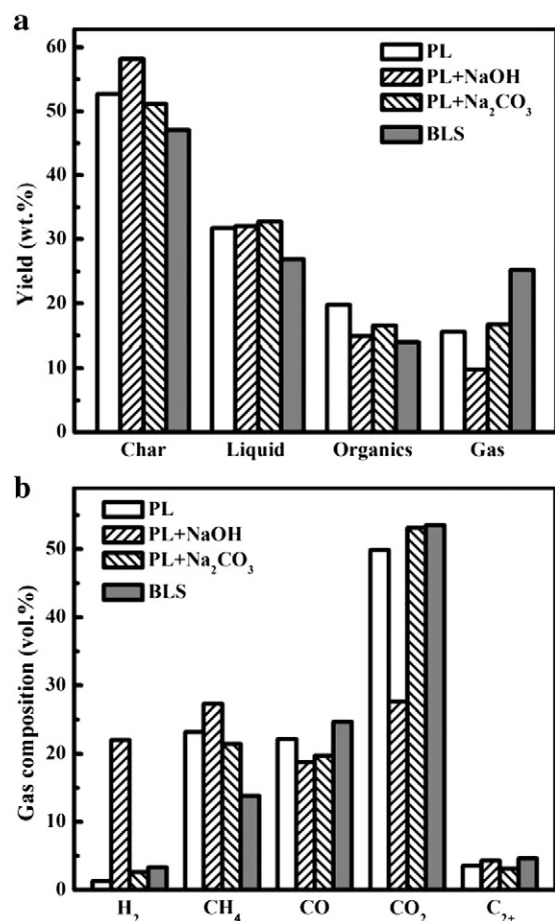


Fig. 9. Comparison of BLS pyrolysis with PL pyrolysis with and without an additive at 450 °C: (a) product distribution and (b) gas composition.

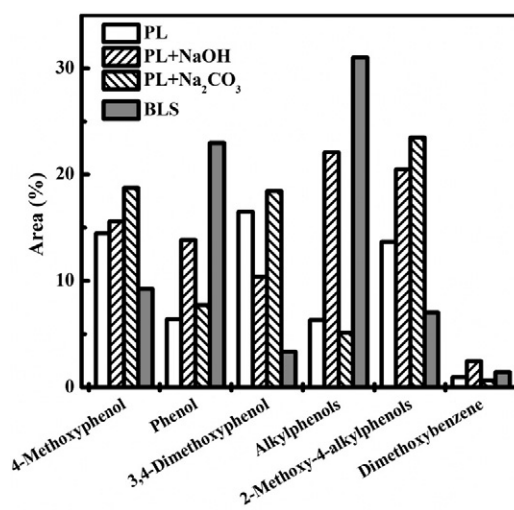


Fig. 11. Major chemicals in tar (organics) from pyrolysis of BLS and PL with and without an additive at 450 °C.

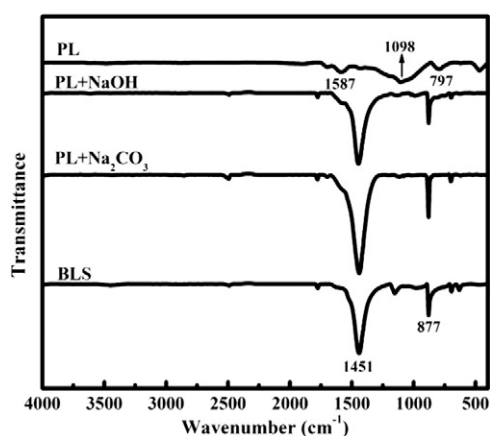


Fig. 12. FTIR spectrum of char from BLS pyrolysis and pyrolysis of PL with and without an additive at 450 °C.

pyrolysis gas composition, the additive other than NaOH did not greatly change the pyrolysis gas composition so that  $\text{CH}_4$ , CO and  $\text{CO}_2$  are the major gas components. Using NaOH greatly increased the  $\text{H}_2$  content from about 3 vol.% to about 20 vol.% and obviously decreased  $\text{CO}_2$  content from about 50 vol.% to about 25 vol.%. These effects should be due to the  $\text{CO}_2$  absorption by NaOH, which is responsible also for the lowest gas yield for the case using NaOH additive.

From Fig. 10 one can see that the tar (organics) from pyrolyzing PL with an additive had much fewer chemical species than the pyrolysis of pure PL. Especially many heavy species with long retention times (above 45 min) disappeared. Overall, the chromatogram for PL pyrolysis with NaOH and  $\text{Na}_2\text{CO}_3$  as its additive are similar to that of BLS pyrolysis. This shows that the formation of different chemicals for pyrolysis of PL and BLS is due to the actions of alkaline ash containing in BLS. Fig. 11 shows further that the use of additives increased the production of phenol chemicals (all types of phenols shown in Fig. 11), which was totally above 80% for the cases with an additive compared to 57% for pure PL. Both NaOH and  $\text{Na}_2\text{CO}_3$  promoted decarboxylation or decarbonylation of aldehydes and ketones and thus resulted in the significant increase in the phenols. With the strong alkaline effect of NaOH, those phenols free of  $-\text{OCH}_3$  (both phenol and alkylphenols in Fig. 11) increased from 13% to 36%. Nonetheless, NaOH also obviously increased the production of 4-methoxyphenol and 2-methoxy-4-alkylphenols. The weak alkaline effect of  $\text{Na}_2\text{CO}_3$  caused the phenols with  $-\text{OCH}_3$  to increase to 60% and the phenols free of  $-\text{OCH}_3$  to remain little changed. This was reasonable to infer that the alkali additives promoted the formation of phenolic products. While the strong alkali led to more phenol and alkylphenols, the weak alkali caused more methoxyphenols.

The spectra of char from PL pyrolysis with and without an additive in Fig. 12 are actually very similar to those shown in Fig. 7 for the pyrolysis of BLS at different temperatures. Because the pyrolysis was at 450 °C, the peaks at  $3430\text{ cm}^{-1}$  and  $1587\text{ cm}^{-1}$  almost completely disappeared from the spectrum of the char for BLS pyrolysis (see also Fig. 7). The FTIR spectra of the chars from pyrolyzing PL with NaOH and  $\text{Na}_2\text{CO}_3$  as the additive are very similar to that of the BLS pyrolysis. Thus, these additives generated the similar effects on PL pyrolysis as the alkaline ash worked on the BLS pyrolysis. For the pyrolysis of pure PL, however, there were still peaks at  $1587\text{ cm}^{-1}$  (carbonyl and carboxyl),  $1098\text{ cm}^{-1}$  (C–O bonds in  $-\text{OCH}_3$  of aryl guaiacyl ether) and  $797\text{ cm}^{-1}$  (C–H in aromatic). It is the effects of the additive which significantly reduced the functional groups at  $1587\text{ cm}^{-1}$ ,  $1098\text{ cm}^{-1}$  and  $797\text{ cm}^{-1}$  in the chars obtained from pyrolyzing PL with an alkaline additive.

## 4. Conclusions

Pyrolysis of dried black liquor (BL), called black liquor solid (BLS), was conducted in a fixed bed reactor at 350–550 °C to experimentally investigate the potential of producing aromatic chemicals from BL. The results showed that high pyrolysis temperature facilitated the break of methoxyl group(s) present in the lignin of BLS, and the highest organics (tar) yield about 14 wt.% was obtained at 450 °C–500 °C. The content of the produced phenols free of  $-\text{OCH}_3$  reached about 60% in addition to a small amount of methoxyphenols including mainly 4-methoxyphenol, 2-methoxy-4-alkylphenol and 3,4-dimethoxyphenol. Comparing to the pyrolysis of purified lignin (PL) from BL at 450 °C (without NaOH or  $\text{Na}_2\text{CO}_3$  additive), the content of phenols (all types) in tar increased to 80 wt.% of the total tar product (organics) if using an alkaline additive (either NaOH or  $\text{Na}_2\text{CO}_3$ ). The result verified that the alkaline additive promoted the formation of phenol chemicals. The strong alkali of NaOH promoted more the production of phenols free of  $-\text{OCH}_3$  including phenol and alkylphenols, while the  $\text{Na}_2\text{CO}_3$  promoted more the formation of methoxyphenols. The heating values of the produced chars from the tested BLS pyrolysis were all higher than 6300 kJ/kg, proving in fact the technical feasibility of cascade utilization for BLS that first pyrolyzes BLS for value-added chemicals (phenols) and in turn combusts its generated char or solid residue to recover energy and alkalis containing in black liquor.

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